

REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-99-

Public reporting burden for this collection of information is estimated to average 1 hour per response, i gathering and maintaining the data needed, and completing and reviewing the collection of information collection of information, including suggestions for reducing this burden, to Washington Headquarters Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Pa

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. R	FINAL 01 Apr 95 to 30 Sep 98
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
CHEMICAL DYNAMICS STUDIES OF REACTIONS IN SOLIDS		F49620-95-1-0310 61102F 2303/FS	
6. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NUMBER	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	
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10. SPONSORING / MONITORING AGENCY REPORT NUMBER		DR MICHAEL R. BERMAN	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION / AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Approved for public release; distribution unlimited.		19990126 050	
13. ABSTRACT (Maximum 200 words)			
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14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT (U)	18. SECURITY CLASSIFICATION OF THIS PAGE (U)	19. SECURITY CLASSIFICATION OF ABSTRACT (U)	20. LIMITATION OF ABSTRACT (UL)

CONTINUE PAGE 2
F49620-95-1-0310/Oklahoma State University

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Final Technical Report
(AFOSR Grant No. F49620-95-1-0310)

CHEMICAL DYNAMICS STUDIES OF REACTIONS IN SOLIDS

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Period Covered:
1 April 1995 to 30 September 1998

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Abstract

The research performed with support by AFOSR grant F49620-95-1-0310 for the period April 1, 1995 to September 30, 1998 is described. Theoretical methods and atomic-level models were developed for studies of fundamental processes and properties of potential HEDM materials. The long-term goal of this research is to perform molecular dynamics and Monte Carlo simulations of the various kinds of processes, including chemical reactions, for systems that display the properties inherent in high-energy high-density materials. This research lays the groundwork for that by providing the theoretical and computational methods as well as accurate molecular and crystal models for important types of energetic systems; for example, molecules such as NTO (5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) and ADN (ammonium dinitramide). Classical dynamics simulations of molecular isomerization in a solid (Ar matrix) were performed for a prototypical energy material (HONO). A significant part of this project was the refinement of chemical dynamics methods for multidimensional problems. A new method was introduced in this work that can be used for accurate treatment of quantum effects such as tunneling in many-atom systems. A fundamental analysis of the failure in some cases of classical mechanics to accurately account for the behavior of zero-point energy was also presented. A method based on simple transition-state theory was developed for computing the rates of mass migration in solids; it was demonstrated for various kinds of atoms in rare gas matrices, and the results are in good agreement with experiment.

I. INTRODUCTION

The objectives of this research program were to develop theoretical methods and perform calculations to investigate fundamental, elementary chemical dynamics processes in systems that can potentially release large amounts of energy upon reaction. The focus was on the dynamics in many-atom systems. The methods developed and used are based on semiclassical mechanics, classical trajectories, and transition-state theory. *Ab initio* quantum mechanical computations were used in developing potential energy surfaces. A significant accomplishment was the development of accurate atomic-level models for NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) and ADN (ammonium dinitramide).

Recent, rapid advances in computational chemistry and computers make feasible atomic-level simulations of complex chemical processes. It is now practical to use *ab initio* quantum chemistry methods to compute information about processes in large systems at an accuracy that is quantitatively predictive. A challenge is to make use of this capability to predict the rates of physical and chemical changes that can occur in complex condensed phase systems. This has been a long-standing goal within our research program, and the purpose of the work performed under this grant was to extend the molecular dynamics methods we have developed to treat rate processes in solid energetic materials while making use of *ab initio* results to the extent possible. Specifically, the work focused on developing accurate intra- and inter-molecular potentials to describe fundamental behaviors of energetic molecules such as NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one), ANTA (5-amino-3-nitro-1,2,4-triazole), and ADN (ammonium dinitramide) with the ultimate goal of performing predictive simulations and calculations pertaining to the sensitivity of these materials. Also, of interest was the development of theoretical methods that can be used to predict the stabilities and structures of novel materials. It is critical that future practical applications of theoretical chemistry be used to make predictions to avoid expensive laboratory work. There is thus a serious need for improved computational methods, and thus a prime aspect of this program was the development of theoretical and computational methods for problems of interest in the HEDM project.

The work described here represents a significant step towards these goals. We have developed methods for formulating global potential energy surfaces to describe both the molecular and crystalline motions as a preliminary step to direct simulations of fundamental processes in energetic materials. We have focused this work on two types of materials: insensitive compounds such as NTO and ANTA and more traditional systems such as ammonium dinitramide (ADN) and ammonium nitrate (AN). The methods developed in this work are readily applicable to other systems, and could be used to predict the properties of novel energetic materials. The storage of energetic molecules in cryogenic matrices has been a prime candidate for the kinds of physical system that may be useful in the development of new, more energetic materials. Thus, we have performed simulations of a prototypical system (HONO) in a rare gas matrix. This study examined the effects of the matrix composition, temperature, and isotopic substitution on the intramolecular isomerization of HONO. Within the context of this same general topic, we have developed a simple theoretical method for computing the rates of atomic diffusion in cryogenic matrices. Some of the concepts in the HEDM program have

involved the storage of metastable species for long times. Thus, when hydrogen is a constituent of the stored molecule tunneling can be important. Prior to our work, methods existed for accurately treating particle tunneling for simple, low-dimensional models. We have developed a semiclassical approach that can be used to accurately predict tunneling rate and that properly includes the multi-dimensional effect. It can be used to treat these potentially important quantum effects in simulations of practical systems of interest in HEDM.

II. Publications

The following is a list of the publications (and manuscripts in preparation for publication) in refereed journals for the grant period:

Paras M. Agrawal, Donald L. Thompson, and Lionel M. Raff,
“Theoretical Studies of the Effects of Matrix Composition, Lattice Temperature and Isotopic Substitution on Isomerization Reactions of Matrix-Isolated HONO/Ar,”
J. Chem. Phys. **102**, 7000-7005 (1995).

Thomas D. Sewell, Yin Guo, and Donald L. Thompson,
“Semiclassical Calculations of Tunneling Splitting in Malonaldehyde,”
J. Chem. Phys. **103**, 8557-8565 (1995).

Yin Guo and Donald L. Thompson,
“Molecular Dynamics and Simple Transition-State Theory Predictions of Rates of Atomic Diffusion in Rare Gas Matrices,”
J. Chem. Phys. **103**, 9024-9029 (1995).

Yin Guo, Thomas D. Sewell, and Donald L. Thompson,
“Analysis of the Zero-Point Energy Problem in Classical Trajectories,”
J. Chem. Phys. **104**, 576-582 (1996).

Dan C. Sorescu, Teressa R. L. Sutton, Donald L. Thompson, David Beardall, and Charles A Wight,
“Theoretical and Experimental Studies of the Structure and Vibrational Spectra of NTO,”
J. Mol. Struct. **384**, 87-99 (1996).

Dan C. Sorescu and Donald L. Thompson,
“Crystal Packing and Molecular Dynamics Studies of the 5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) Crystal,”
J. Phys. Chem. B **101**, 3605-3613 (1997).

Dan C. Sorescu, Carl M. Bennett, and Donald L. Thompson,
"Theoretical Studies of the Structure, Tautomerism, and Vibrational Spectra of 5-Amino-3-nitro-1,2,4-triazole (ANTA),"
J. Phys. Chem. A, **102**, 10348-10357 (1998).

Dan C. Sorescu and Donald L. Thompson,
"Classical and Quantum Mechanical Theoretical Studies of the Ammonium Dinitramide (ADN) Crystal,"
In preparation.

The following is a list of review articles and book chapters written by the PI during the grant period. These cover work partially supported by this grant.

Thomas D. Sewell and Donald L. Thompson,
"Classical Trajectory Methods for Polyatomic Molecules,"
Int. J. Mod. Phys. B, **11**(No. 9), 1067-1112 (1997).

Yin Guo and Donald L. Thompson,
"Multi-Dimensional Semiclassical Tunneling,"
in *Methods in Multidimensional Molecular Dynamics*, edited by D. L. Thompson (World Scientific Pub., New Jersey, 1998).

Donald L. Thompson,
"Classical Trajectory Simulations of Molecular Collisions,"
in *Encyclopedia of Computational Chemistry*, edited by H. F. Schaefer III, (John Wiley & Sons, New York, 1998).

III. Brief Summaries of the Completed Research:

a. Atomic Diffusion in Rare-Gas Matrices

We have shown that a simple transition-state theory (STST) can be used to accurately predict classical rates of atomic diffusion in rare-gas matrices. We compared the results of STST and molecular dynamics (MD) for H-atom and C-atom diffusion in argon matrices. The results are in good agreement. The use of STST provides an considerable savings in computation time and in the amount of information about the potential needed compared with a MD or MCTST treatment. The STST calculations can be readily calculated by using only information about the system at equilibrium and the transition state. A further advantage of the STST approach is that the accuracy improves as the temperature decreases, but not the difficulty of the calculations. Molecular dynamics simulations become more expensive as the temperature decreases.

We have also computed rates for H-, C- and O-atoms in xenon matrices and compared the results with the experimental results of Weitz and coworkers [J. Chem. Phys. **96**, 2846 (1992) and Chem. Phys. Letters **211**, 430 (1993)]. These comparisons tend to support the conclusion that there are defects present in the lattices in the experiments. While we have not done the calculations in this study, it should be possible to use STST with reasonable assumptions about lattice defects to carry out a study in which one develops a model (or models) of imperfect lattices that give agreement with the measured diffusion rates. Since we have shown that STST is valid for these processes, such a study should lead to an understanding of the nature of the lattices that leads to the various reported experimental data for atomic diffusion in rare gas matrices.

b. Molecular Isomerization in Rare-Gas Matrices

Classical dynamics calculations were carried out to study the effects of matrix composition, lattice temperature, and isotopic substitution on *cis-trans* isomerization rates and the rates of vibrational energy transfer to the lattice phonon modes for HONO, DONO, and H¹⁸ON¹⁸O in argon matrices. The matrix-isolated isomerization rates are greater than those computed for the isolated molecules. This is attributed to a vibration→lattice motion→rotation→torsion energy transfer mechanism that enhances the isomerization rate. The isomerization process in the matrix is nonstatistical, that is, it displays vibrational mode specificity. In the gas phase (isolated molecules), D and ¹⁸O substitution produce small, positive changes in the isomerization rate (13% and 26%, respectively) due to increased kinetic coupling to the torsional mode. In the matrix, however, the isotope effects are negative and of greater magnitudes. This is attributed to reduced rates of energy transfer from the lattice to rotation of the isotopic molecules, which have greater moments of inertia.

c. Treating Zero-Point Energy in Classical Trajectories

One of the potential problems with classical trajectories is a physical flow of zero-point energy (ZPE). Quantum mechanically, within the normal mode approximation, each molecular mode is expected to contain an amount of energy at least equal to the ZPE of that mode. However, in a classical mechanical simulation of a molecule the energy can flow without this restriction among the modes yielding behavior that does not correspond to that of the real system. Recently, various methods to correct this “problem” have been suggested. Two general approaches are being used. In the “passive” methods nothing is done to alter the classical mechanics but the trajectories which violate ZPE criteria are discarded. Several “active” methods have been devised where the equations of motion are modified by the incorporation of some kind of constraint which prohibits individual trajectories from exploring regions of phase space where mode energies are less than the ZPE. The active methods can cause damage to the dynamics as we have previously shown for one of them [Sewell *et al.*, Chem. Phys. Lett.

193, 512 (1992)]. In addition to this, however, is the fact that they are all based on an invalid assumption, that is, that individual trajectories should obey the ZPE criterion. In the semiclassical limit there is a one-to-one correspondence between the invariant tori in phase space and quantum mechanical eigenvalues. This correspondence is the basis of the classical trajectory method; it is assumed that an ensemble average of points on a torus corresponds to the expectation value of an observable of the quantum state. Thus, methods for correcting “the ZPE problem” that hold individual trajectories to the quantum mechanical restrictions violate this correspondence. Quantum mechanically it is the mean value of the Hamiltonian for a given state that cannot be less than the ZPE and, correspondingly, it is the ensemble-averaged mode energies in the classical trajectories that should be expected (or required) to obey the ZPE constraints. We have used the Henon-Heiles Hamiltonian, for which quantal calculations are feasible, to illustrate the problems of several of the proposed methods for dealing with the “ZPE problem.”

d. Semiclassical Treatment of Multi-Dimensional Tunneling

Proton tunneling in polyatomic systems is sensitive to the motions of the heavy atoms. The collective motions of the heavy skeletal atoms can lead to significant variations in the height and width of the barrier through which the tunneling occurs. Thus, selective excitation of various vibrational modes of a molecule can cause large differences in tunneling rates or tunneling splittings. We have been investigating these effects and the methods for treating them [Chem. Phys. Lett. 193, 347 (1992); J. Chem. Phys. 100, 6445 (1994); Chem. Phys. Lett. 224, 470 (1994)]. We are interested in treating the full dimensionalities of many-atom systems; thus we have been using semiclassical techniques in which JWKB tunneling probabilities are calculated at turning points in the “tunneling coordinate” along classical trajectories.

Tunneling splitting of the ground state of malonaldehyde serves as an excellent case for these studies because of the availability of experimental results. We will present the results of calculations in which all 9 atoms are allowed 3-D motion. The computed splitting of the pure ground state is in good agreement with the experimental value. We have also studied the effects of exciting each of the normal modes on the ground state splitting. These results show that the heavy atom motions have significant influence on the tunneling.

e. NTO Equilibrium Structure, Force Field, and Vibrational Spectra

We have initiated studies of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one). Working in collaboration with Prof. Charles Wight and Mr. David Beardall, University of Utah, we have characterized the structure and potential energy surface near equilibrium. The experimental frequencies determined from infrared spectra of pure NTO thin films as well as for NTO molecules isolated in an argon matrix at 21 K. We computed corresponding information for the isolated molecule at the MP2/6-311G** level using the Gaussian-92 program. A force field was then developed on the basis of the theoretical

and experimental results. The experimental vibrational frequencies for NTO films together with scaled fundamental frequencies from the *ab initio* calculations were used to construct a force field for NTO in the solid phase.

The calculated fundamental frequencies for these potentials are in good agreement with the experimental values for thin film and matrix-isolated conditions. The differences in the positions of the spectral bands indicate that environment and preparation procedure have a marked influence on the spectral characteristics of NTO.

f. NTO Crystal Model

We have also developed an intermolecular potential that describes the structure of the β -form of the NTO crystal. The potential is composed of pairwise atom-atom Lennard-Jones (6-12), hydrogen-bonding Lennard-Jones (10-12), and Coulombic charge-charge interactions. Crystal packing calculations were performed to determine the equilibrium crystallographic structure and lattice energy for the model. Further testing of the intermolecular potential was done by performing isothermal-isobaric MD (molecular dynamics) calculations at ambient pressure for temperatures in the range 4.2 to 400 K. The calculated results reproduce to within 2-6% the measured cell dimensions of the NTO crystal at 300 K. Little rotational or translational disorder occurs in the thermal simulations for the model.

By combining the intramolecular and intermolecular potentials which we have developed, predictions of non-reactive processes in the β - NTO crystal are possible. It also provides the basis for a potential that includes the forces for chemical reactions.

g. Ammonium Dinitramide

One of our prime interests is the development of models to describe the full range of energetic materials. Ionic compounds present some of the more difficult problems. We have considered ammonium nitrate and ammonium dinitramide (ADN), primarily the latter.

We have performed plane-wave *ab initio* calculations based on density functional theory and the pseudopotential method to investigate the structural properties of ADN crystal. The optimization of the crystal structure has been done with full relaxation of atomic positions and lattice parameters. The periodic nature of the crystal has been considered in calculations by employing periodic boundary conditions in all three directions. The predicted crystal structure was found in good agreement with X-ray crystallographic data and indicates no internal symmetry for the dinitramide ion, in contradistinction to the gas phase MP2 results.

We have developed an intermolecular potential for ADN crystal in the approximation of rigid molecules. This potential contains 6-12 and 10-12 potential terms (for hydrogen bonding). The electrostatic charges assigned to different atoms of the molecules have been determined based on the fit to the *ab initio* calculated electrostatic

potential. The intermolecular potential was fitted to reproduce the crystallographical parameters and the lattice energy.

A first set of tests of this potential was done using molecular packing calculations without symmetry constraints. The predicted lattice parameters are reproduced with a maximum deviation of 1.88%. The predicted lattice energy is 607.9 kJ/mole while the estimated lattice energy by Politzer [P. Politzer, J. M. Seminario, and M. C. Concha, *J. Molec. Struct. (Theochem)* **427**, 123 (1998).] is 602.5 kJ/mole.

Further tests of this potential were done using isothermal-isobaric molecular dynamics simulations in the temperature range 4.2-350 K. It is found that the main temperature effects consist in the increase of rotational disorder of the ammonium ions without any significant change of the translational order of the ionic species, in agreement with experimental findings (R. Gilardi, private communication).

h. Ammonium Nitrate

A long-standing problem concerns the phase transitions in ammonium nitrate (AN). There are five crystal phases of AN over the temperature range -18 to 170 °C. Of particular importance are the transitions between phases III and IV that occur near 32 °C. The phase transitions result in undesirable changes in the properties of the material and its performance in energetic materials applications. We have initiated studies to investigate the fundamental changes that can occur in crystalline AN. The goal is to develop models that can be used to simulate these phases transitions. We are continuing this work by performing *ab initio* studies of isolated AN molecules.

IV. GRANT PERSONNEL

The personnel who worked on this project are:

Professor Donald L. Thompson, Principal Investigator

Dr. Yin Guo, Postdoctoral Research Associate

Dr. Dan C. Sorescu, Postdoctoral Research Associate

Dr. Angela Wilson, Postdoctoral Research Associate

Mr. Gary Thacker, Graduate Assistant

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Mr. Justin Krouse, Graduate Assistant (Supported by an ASSERT augmentation grant.)